Kinetics of Sodium Borohydride Hydrolysis in Aqueous-Basic Solutions

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Abstract

Liquid-phase catalytic hydrolysis of sodium borohydride ($NaBH_4$) for hydrogen production necessitates long-term stability of base-stabilized $NaBH_4$ solutions at higher temperatures. The present paper reports the kinetics of aqueous-basic solutions containing 20 wt% $NaBH_4$ with 1-15 wt% sodium hydroxide (NaOH) at 80 ^{0}C. The established kinetic model employs a modified isoconversional method assuming single-step kinetics. The estimation of kinetic parameters is performed by gPROMS (general PRocess Modeling System) parameter estimation tool. The reaction kinetics differs from low to highly-concentrated NaOH solutions. In highly-basic (≥10 wt% NaOH), aqueous solutions of $NaBH_4$, the rate is independent of NaOH concentration, while for lower-basic (< 10 wt% NaOH) solutions, the dependence is -0.57, confirming the inhibition of hydrolysis kinetics by NaOH.

Keywords: *Sodium borohydride, Hydrogen production, Isoconversional method, gPROMS, Kinetics*

1 Introduction

Catalytic hydrolysis of aqueous sodium borohydride ($NaBH_4$) solutions has been widely accepted as a potential technology for delivering H_2 gas (eq.1) to fuel cells due to its high theoretical hydrogen storage capacity (10.9 wt%) and safe operation. Aqueous solutions of $NaBH_4$ undergo self-hydrolysis even at low temperature. An increase in solution pH inhibits the hydrolysis reaction rate and the conventional catalytic hydrolysis is generally carried out on sodium hydroxide (NaOH) stabilized solutions.

$$NaBH_4 + (2+x)H_2O \xrightarrow{\text{catalyst}} NaBO_2.xH_2O + 4H_2 + \text{heat} \quad (1)$$

The stability of aqueous borohydride solution increases with base concentration. However, elevated temperatures and long-term storage decrease the stability, and this should be carefully considered during the handling and storage of these solutions [1-2]. The rate dependence of pH and mechanistic details were extensively studied in 1960s and 1970s in controlled buffer solutions [2]. The hydrolysis kinetics differ from low pH (<12) to high pH. In the pH range of 7.7-9.5, there is first-order dependence on both borohydride and hydrogen ion concentration. However, the rate becomes less sensitive to hydrogen ion concentration with an increase in pH and the order decreases to about 0.4 at very high pH (>12). These models were established for very dilute buffered $NaBH_4$ solutions (< 0.5 wt %) at low to medium temperatures (15-35 ^{0}C), which are very restrictive conditions for practical applications.

Churikov et al. [3] studied the influence of medium to high temperatures (50-100 ^{0}C) and high initial pH (12.5-14.5) on the hydrolysis rate of dilute $NaBH_4$ solutions (0.15 wt% to 3 wt%). The established kinetic model for conversions up to 30% comprises two parts. The first part represents the high pH range (>12), where the hydrolysis rate is independent of pH, and the second part represents the low pH range (<12) where the hydrolysis rate increases with decrease in pH. This model besides being developed for diluted $NaBH_4$ solutions, exhibits some limitations deriving from: (1) assumption of first-order dependence on borohydride concentration throughout the reaction in all the studied temperatures; and (2) reaction order greater than unity (1.79) regarding hydrogen ion concentration. Most recently, Bartkus et al. [4] established two semi-global rate equations describing the consumption rate of $NaBH_4$ and hydrogen ion based on extensive experimental kinetic data (0.0 wt% to 25 wt% $NaBH_4$, 0.0 wt% to 4.0 wt% NaOH and 25^{0}C to 75 ^{0}C). The rate expression for hydrogen ion, which is a major contribution of this work is empirical and does not allow, therefore, gaining further theoretical insight on the influence of pH on the self-hydrolysis kinetics.

The present work reports the kinetic study of aqueous concentrated $NaBH_4$ solutions (20 wt %) containing 1-15% NaOH at higher temperature (80 ^{0}C) by a modified isoconversional method. The objective is to determine the hydrogen loss during the handling and storage of aqueous-basic solutions of $NaBH_4$ under practical applications.

2 Experimental

The experimental kinetic data used in the present study are those reported by Yu and Matthews [5]. The evolution of metaborate formation and $NaBH_4$ consumption were characterized *in-situ* by ^{11}B nuclear magnetic resonance (NMR) technique for NaOH-stabilized $NaBH_4$ solutions. The details of the experimental runs in terms of NaOH concentration, duration of the experiments and conversion at the end of the experiments are given in Table 1. As can be seen, the final conversion decreases with increase in NaOH concentration, confirming that NaOH inhibits the hydrolysis reaction.

Table 1. Details of Hydrolysis Experiments for 20 wt% $NaBH_4$ solutions at 80 ^{0}C.

NaOH (wt%)	Duration (hr)	Final $NaBH_4$ Conversion (%)
0	24.0	98.00
1	25.0	81.00
5	18.5	41.30
10	24.5	30.70
15	23.0	5.40

3 Modelling

The kinetics of complex heterogeneous processes that are stimulated by change in temperature is generally described by isoconversional method assuming single-step [6]. This method provides deconvolution of multi-step reactions and enables modelling the reaction kinetics without a deeper insight into its mechanism. This model-free isoconversional method is considered to produce consistent kinetic results from isothermal and non-isothermal experiments. The present study employs this approach for the complex homogeneous $NaBH_4$ hydrolysis kinetics.

The isoconversional method by single-step kinetic approximation is expressed as [6]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_{ap}(T)\, f(\alpha) \qquad (1)$$

where α is the extent of conversion, t the time, $k_{ap}(T)$ the apparent rate constant dependent on temperature *T*, and $f(\alpha)$ the conversion function representing the process mechanism.

Equation (1) intrinsically assumes constant reaction mechanisms throughout the process and the mechanism of the process is solely a function of conversion and independent of any temperature or temperature regime [6]. This may not hold true in the case of highly complex reaction such as $NaBH_4$ hydrolysis. The present work attempts to address this issue by using a model-based isoconversional method, which has the potential to capture the change in mechanism of the process during the progress of reaction, as well as with temperature or temperature regime.

The $NaBH_4$ hydrolysis process exhibits its maximum rate at the beginning of the reaction, which decreases continuously with the extent of conversion. The most appropriate form of $f(\alpha)$ for such decelerating type process is the 'reaction-order model' which is of the form [6]:

$$f(\alpha) = (1 - \alpha)^m \qquad (2)$$

where *m* is the apparent reaction order with respect to $NaBH_4$ concentration.

Assuming the above 'reaction-order model', the rate expression for NaOH-stabilized solutions can be written as:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_{ap}(T)\; C_{0,\mathrm{NaBH_4}}^{m\text{-}1} (1\text{-}\alpha)^m C_{\mathrm{NaOH}}^{n} \qquad (3)$$

where $C_{0,\mathrm{NaBH_4}}$ is the initial concentration of $NaBH_4$, C_{NaOH} the initial concentration of NaOH, and *n* the apparent reaction order with respect to NaOH concentration.

The parameter estimation objective function is based on maximum likelihood estimation (MLE), a popular statistical method used in a large variety of applications. The optimization of the parameter estimation objective function is performed by the parameter estimation tool of gPROMS 3.1.3. (general PRocess Modeling System), an advanced process modeling software by Process System Enterprise (PSE) for simulation, optimization and parameter estimation (both steady-state and dynamic) of highly complex processes. The MXLKHD solver based on maximum likelihood approach is used, where the global optimum is found by applying a sequential quadratic programming (SQP) method. The MXLKHD solver calls the DASOLV solver for the solution of the kinetic model comprising the differential algebraic equations. Besides rapid estimation of the parameters, the powerful numerical method provided by gPROMS allows rigorous statistical testing of the estimated parameters for uncertainty in the values and the model validation, i.e. how effectively the model represents the system.

4 Results and Discussion

4.1. Parameter Estimation

The goal was to estimate k_{ap}, *m* and *n* for a predefined conversion and investigate the effect of the extent of conversion on the estimated parame-

Table 2. Estimated Parameters for 20 wt% $NaBH_4$ solutions containing various concentrations of NaOH at 80 ^{0}C.

NaOH (wt%)	Parameter	Conversion (%) 5	10	15	20	40	Mean
0	k_{ap}	0.51±0.004	0.46±0.001	0.41±0.008	0.32±0.009	0.11±0.04	-
	m	0.27±0.001	0.25±0.030	0.26±0.003	0.28±0.006	0.28±0.01	0.268±0.01
1, 5	k_{ap}	0.043±0.003	0.046±0.001	0.043±0.01	0.045±0.02	0.038±0.03	0.043±0.02
	m	1.010±0.150	0.990±0.150	1.020±0.11	0.990±0.10	1.110±0.09	1.020±0.12
	n	-0.59±0.040	-0.56±0.060	-0.55±0.07	-0.580±0.04	-0.57±0.05	-0.57±0.05
10	k_{ap}	0.012±0.008	0.013±0.001	0.009±0.002	0.010±0.005	-	0.011±0.004
	m	0.980±0.050	0.970±0.170	1.080±0.002	1.040±0.001	-	1.018±0.060
	n	0.031±0.001	0.019±0.008	0.003±0.002	0.002±0.001	-	0.014±0.003
15	k_{ap}	0.004±1.6E-6	-	-	-	-	-
	m	0.960±0.080	-	-	-	-	-
	n	0.008±0.0002	-	-	-	-	-

ters. This demands experimental conversions above the pre-defined conversion on different initial NaOH concentrations. As seen in Table 1, 15 wt% NaOH solutions give 5.4% conversion; implying the maximum possible conversion for parameter estimation using 0, 1, 5, 10 and 15 wt % NaOH solutions to be 5.4%. Therefore, as a first step, the conversion is fixed at 5% and an attempt made to estimate the parameters using all the solutions. It was not possible to optimize the parameter estimation objective function using the 5 sets of kinetic data. Hence a number of systematic optimization runs has been carried out using different combinations of experimental kinetic data and conversions. If the number of experimental points was not sufficient to carry out the parameter estimation by gPROMS, they are generated by interpolating the polynomial of conversion-time data fitted by least squares fitting procedure (R^2 > 0.99). The converged solution is obtained for: (1) 0-40% conversion using 0 wt% NaOH solution; (2) 0-40% conversion, using 1 and 5 wt% NaOH solutions together; (3) 0-20% conversion for 10 wt% NaOH solution; and (4) 0-5% conversion using 15 wt% NaOH solution.

The results obtained with 95% confidence level are tabulated in Table 2. As seen, the value of the rate constant decreases for non-stabilized solutions, while it remains constant for stabilized solutions during the progress of reaction. The reaction order with respect to borohydride concentration, even though remaining constant throughout the reaction, displays different values for non-stabilized and stabilized solutions. These clearly points out to diverse reaction kinetics. The present study focuses on stabilized solutions and non-stabilized solutions are not discussed any further.

The reaction kinetics is first-order in borohydride concentration in all the studied stabilized solutions. However, the dependence of NaOH differs from low to high concentrations. In highly concentrated solutions of NaOH (≥10 wt %), the rate is independent of NaOH concentration, while in low concentrations (< 10 wt %), the value of n is -0.57. The value of the rate constant decreased from 0.043 to 0.004 with an increase in NaOH concentration from 1 to 15 wt%. However, the value of k_{ap} is found to remain constant with an increase in extent of conversion, thus suggesting that the solution properties remain approximately constant during the progress of reaction.

The comparison of experimental with model predicted performance using estimated parameters (Table 2) is carried out for all the experimental runs. The comparison for 1, 5 and 10 wt% NaOH solution for 15% conversion is illustrated in Figure 1. Similar trends are observed in all the other cases investigated. The good agreement found between experimental and model predicted performances demonstrates that the estimated parameters can be used to satisfactorily correlate (reproduce) the experimental kinetic data from which these parameters have been estimated.

4.2. Kinetic Model

The reaction kinetics of NaOH-stabilized solutions of $NaBH_4$ depends on NaOH concentration. The reaction rate in lower-basic aqueous solutions (< 10 wt% NaOH) follows the following power-law model.

$$\frac{d\alpha}{dt} = k_{ap}(T)(1-\alpha)\, C_{\mathrm{NaOH}}^{-0.57} \qquad (4)$$

In highly-basic aqueous solutions (≥10 wt% NaOH) of $NaBH_4$, the rate can be described by:

$$\frac{d\alpha}{dt} = k_{ap}(T)(1-\alpha) \qquad (5)$$

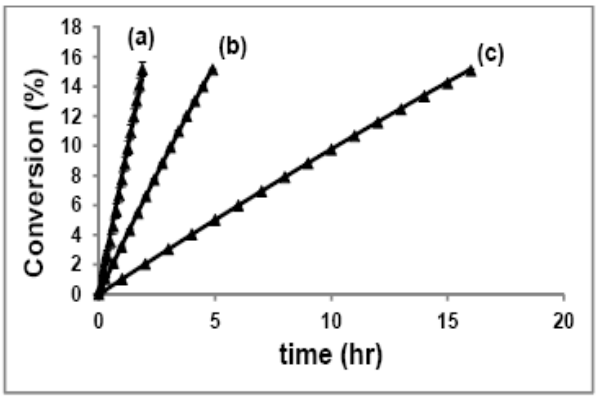

Fig. 1. Comparison of model prediction with measurements for 20 wt% $NaBH_4$ solution at 80 ^{0}C and 15% conversion: (a) 1 wt% NaOH; (b) 5 wt% NaOH, (c) 15 wt% NaOH. Markers: measured values; solid line: predicted values

It is worthwhile noting that earlier studies using buffered diluted $NaBH_4$ solutions (< 1 wt %) at low to medium temperature (15-35 ^{0}C) reported first-order dependence in borohydride concentration [2]. The dependence of NaOH concentration on catalytic hydrolysis of $NaBH_4$ using different catalysts is studied by various authors [2]. These studies show that the reaction rate is not only dependent on NaOH concentration, but also on the type and nature of the catalysts.

Demirci and Garin [7] investigated the kinetics of hydrolysis of NaOH (0.4-5 wt %) stabilized diluted $NaBH_4$ solutions (0.5-3 wt %) at 8-24 ^{0}C, over Ru (1 wt%)-promoted sulphated zirconia (Ru-SZ) catalyst and observed a -0.35 dependence in NaOH. Zhang et al. [8] reported a reaction order of -0.54 in NaOH for 5 wt% $NaBH_4$ solution containing 1-10 wt% $NaBH_4$ using Zr/Co/C catalyst at 25 ^{0}C. The NaOH inhibits the reaction rate over these catalysts and thus displays a negative reaction order. In the present study the obtained negative dependence in low concentration and zero dependence in high concentration confirm the observed rate inhibition by NaOH.

Bartkus at al. [4] showed first-order dependence in borohydride concentration and -0.79 order in NaOH concentration for 0.5 wt% to 25.0 wt% $NaBH_4$ and using 0.0 wt% to 4.0 wt% NaOH at 25 ^{0}C to 75 ^{0}C. The difference in NaOH dependence between Bartkus at al. and the present study is most likely due to the coupling of the hydrogen ion concentration between the rate expressions of $NaBH_4$ consumption and hydrogen ion depletion in their model.

5 Conclusions

A kinetic study based on model-based iso-conversional method assuming single-step kinetics has been carried out on aqueous-basic solutions of $NaBH_4$ with the aim of predicting hydrogen release during the handling and storage of these solutions. This method enables modelling of the hydrolysis process without deeper insight into its mechanism. The kinetic parameters with statistically significant values were estimated by gPROMS parameter estimation tool using ^{11}B NMR kinetic data.

The study on concentrated $NaBH_4$ solution (20 wt%) containing various concentrations of NaOH (1 wt%, 5 wt%, 10 wt% and 15 wt%) at high temperature (80 ^{0}C) for 0-40% conversions shows a variation in reaction kinetics from low to high NaOH concentration. For lower-basic aqueous solutions of $NaBH_4$, the reaction rate is inhibited by NaOH and the reaction kinetic is -0.57 dependence in NaOH concentration and first-order dependence in $NaBH_4$. In highly-basic solutions of $NaBH_4$, the reaction rate is independent of NaOH concentration and the reaction kinetic is zero-order dependence in NaOH concentration and first-order dependence in $NaBH_4$ concentration.

There is a good agreement between the measured and model predicted values in all the studied solutions. This allows predicting the transient hydrogen loss for storage purposes.

6 References

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